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(19)

(72) The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of The Patents Act 1949 are OLE WØRTS, a Swedish subject of 7, Akselsvej, DK-3660 Stenløse, Denmark and POUL LINDGREEN, a Danish subject of 63, Engholmvej, DK-4000 Roskilde, Denmark

(54) IMPROVEMENTS IN OR RELATING TO A PROCESS FOR COATING WATER SOLUBLE OR WATER DISPERSIBLE PARTICLES BY MEANS OF THE FLUID BED TECHNIQUE

(71) We, NOVO INDUSTRI A/S, formerly known as Novo Terapeutisk Laboratorium A/S, a Danish company of Novo Alle, DK-2880 Bagsvaerd, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for coating water soluble or water dispersible particles by means of the fluid bed technique.

It is known to coat various particulate products having a particle size of less than about 10 mm, preferably less than 1 mm, in order to minimize dust formation, e.g. enzyme containing additives for detergent compositions in powder form. However, considerable difficulties have been experienced in performing this coating. In practice it has hitherto been usual to utilize coating agents dissolved in organic solvents rather than in water when coating water soluble particles. The organic solvents have to be evaporated and recovered at a later stage of the process and may, furthermore, create a fire hazard and environmental problems. If, on the other hand, the organic solvent is not recovered, the coating process works in an uneconomical way.

Also, it is known to utilize the fluid bed technique to coat various water soluble or water dispersible particles by atomization of aqueous solutions of film forming, water soluble coating agents, this process being described in Wurster's USA Patent No. 3,196,827. However, in this known process, it is difficult to avoid agglomeration of the particles to be coated, and it is mentioned that this known process is only suited for particles bigger than 30 mesh (ab. 0.6 mm). Also, by using Wurster's method it is difficult to obtain thin coatings.

We have now found that it is possible to utilize an aqueous liquid for coating particulate products having a particle size of less than about 1 mm (mean diameter in the range of from 0.1 to 0.6 mm) in a fluid bed process whereby particles can be coated with an extremely thin coating and without substantial danger of agglomeration.

According to the present invention there is provided a process for coating water soluble or water dispersible particles by means of the fluid bed technique, which process comprises introduction of the particles to be coated in a fluid bed reactor the mean diameter of the particles to be coated being in the range of from 0.1 mm to 0.6 mm, and introduction of a coating material essentially consisting of an aqueous solution or dispersion of a macromolecular film forming, water soluble or water dispersible coating agent by means of atomization, wherein the relative humidity of outlet air from the fluid bed is below 100% and wherein the maximum size of the atomized droplets of the coating fluid does not exceed the minimum size of the particles to be coated.

If the maximum size of the atomized droplets of the coating fluid exceeds the minimum size of the particles to be coated, agglomeration will occur.

Thus, by means of the invention, agglomeration can be avoided, and it is possible to perform the coating with a layer as thin

as 0.1—10 μ, in a preferred embodiment 0.5—1 μ, corresponding to about 1% of the dry particle weight. For a given thickness of the layer of coating agent a larger amount of coating agent, calculated on the particle weight, will be used with decreasing particle size. This will appear from the following Table I.

TABLE I

Amount of coating agent, calculated as per cent by weight of the particles to be coated

Thickness of coating	Alcalase P Mean diameter of particles 400 μ	Alcalase M Mean diameter of particles 700 μ
0.5 μ	0.8%	0.5%
1.0 μ	1.5%	0.9%

Although the coating produced according to the invention in a preferred embodiment is very thin it is, according to the invention, also possible to produce coatings as thick as about 100 μ, if desired.

The minimum size of the particles to be coated can be determined by sieve analysis, and the maximum size of the atomized droplets of coating fluid can be read from charts available from the manufacture of the nozzle, when the viscosity of the fluid and the pressure is known.

In a preferred embodiment of the process according to the invention the water soluble or water dispersible particles to be coated contain one or more enzymes, for example proteases, amylases, lipases or celluloses.

In another preferred embodiment of the process according to the invention the enzyme or enzymes are bacterial proteinases.

In another preferred embodiment of the process according to the invention the bacterial proteinases are precoated in order to reduce dust formation.

In another preferred embodiment of the process according to the invention the bacterial proteinases are microbial proteinases such as Alcalase P or Alcalase M or are alkaline resistant proteinases manufactured according to British Patent No. 1,243,784.

Alcalase, which is a trade mark belonging to Novo Industri A/S, is a microbial proteinase. Alcalase P is a prilled Alcalase. Alcalase M is Alcalase which is treated by means of a Marumerizer as described in our co-pending British patent application No. 36564/70 (Serial No. 1,362,365) and in our published French Patent No. 2,099,349. The word "Marumerizer" is a Trade Mark.

In another preferred embodiment of the process according to the invention, the enzyme or enzymes are bacterial or fungal carbohydrases.

In another preferred embodiment of the process according to the invention, the bacterial amylases are thermally stable amylases manufactured according to British Patent No. 1,296,839.

In another preferred embodiment of the process according to the invention, the macromolecular film forming, water soluble or water dispersible coating agent is a cellulose derivative.

In another preferred embodiment of the process according to the invention, the cellulose derivative is methyl cellulose, hydroxybutylmethyl cellulose, sodium carboxymethyl cellulose, hydroxyethylmethyl cellulose or hydroxypropylmethyl cellulose.

In another preferred embodiment of the process according to the invention, the macromolecular film forming, water soluble or water dispersible coating agent is a polyvinylpyrolidone.

In another preferred embodiment of the process according to the invention, the macromolecular film forming, water soluble or water dispersible coating agent is a polyethylene glycol, preferably of a molecular weight in the range of from 400 to 6000.

In another preferred embodiment of the process according to the invention, the macromolecular film forming, water soluble or water dispersible coating agent is a methacrylic resin.

In another preferred embodiment of the process according to the invention, the macromolecular film forming, water soluble or water dispersible coating agent is gelatine.

In another preferred embodiment of the process according to the invention, the coating fluid contains a plasticizer.

In another preferred embodiment of the process according to the invention, the plasticizer is a glycerol.

In another preferred embodiment of the process according to the invention, the glycerol is used in an amount of up to 60% of the dry weight of the coating agent, preferably in an amount in the range of from 10 to 30% of the dry weight of the coating agent.

In another preferred embodiment of the process according to the invention, the concentration of the macromolecular film forming, water soluble or water dispersible coating agent in the coating fluid is in the range of from 2 to 50 weight-%.

In another preferred embodiment of the process according to the invention, the con-

centration of the macromolecular film forming, water soluble or water dispersible coating agent in the coating fluid is in the range of from 4 to 10 weight-%.

In another preferred embodiment of the process according to the invention the mean diameter of the particles to be coated is in the range of from 0.2 to 0.6 mm.

In another preferred embodiment of the process according to the invention, the thickness of the coating layer is in the range of from 0.1 to 10 μ.

In another preferred embodiment of the process according to the invention, the thickness of the coating layer is in the range of from 0.5 to 1μ.

The process according to the invention can be carried out in a continuous manner as well as batchwise. However, in a preferred embodiment of the invention the process is carried out batchwise. In all the following Examples, the process is carried out batchwise.

The invention also encompasses a coated product comprising coated water soluble or water dispersible particles, whenever prepared by means of the process according to the invention.

The water soluble or water dispersible particles can be of any material which, for any reason, is to be coated. Examples of materials encompassed are enzyme additives, for example, proteolytic enzyme additives for detergents, particulate medicaments, for example oral penicillin preparations, or hygroscopic substances, for example fertilizers.

Coating of the particles is carried out for various reasons, for example, in order to minimize dust formation, to protect against ultra-violet radiation, humidity or acidity or to minimize contamination.

The coating agent can be any macromolecular film forming, water soluble or water dispersible coating agent, for example:

Methocel MC 15: methyl cellulose of a methoxyl DS (Degree of Substitution) of 1.64 to 1.92 and of a DP (Degree of Polymerization) corresponding to viscosities from 8 cP to 10,000 cP in a 2% aqueous solution at 20°C. The Word "Methocel" is a Trade Mark.

Tylose C 10: sodium carboxymethyl cellulose of a DS from 0.4 to 1.5 and a DP from 50 to 1000. The word "Tylose" is a Trade Mark.

Tylose MH 20: methylhydroxyethyl cellulose (or hydroxyethylmethyl cellulose) of a methoxy DS from 1.0 to 2.0, a hydroxyethyl DS from 0.1 to 0.5 and a DP from 50 to 1000.

Methocel XD 1181: hydroxypropylmethyl cellulose of a methoxyl DS from 1.0 to 2.0, a hydroxypropyl DS from 0.1 to 0.5, and a DP from 50 to 1000.

Kollidon K 25 PVP: polyvinylpyrrolidone of an average molecular weight of 10,000, 40,000, 160,000 and 360,000 and mixtures thereof resulting any intermediate average molecular weight and mixtures or single components modified with plasticizers such as carboxymethyl cellulose and cellulose acetate. The word "Kollidon" is a Trade Mark.

Carbowax: polyethylene glycols of average molecular weight of 400, 600, 1000, 1540, 4000, 6000 and mixtures thereof any intermediate average molecular weight. The word "Carbowax" is a Trade Mark.

Eudragit E 30 D: methacrylic resins, aqueous dispersions thereof. This tablet lacquer is completely insoluble in alkaline liquids. The word "Eudragit" is a Trade Mark.

Solugel: gelatine. The word "Solugel" is a Trade Mark.

Polypropylene glycols.

Polyvinyl alcohols.

Alginates.

The concentration of the coating agent in the aqueous or substantially aqueous solution or dispersion corresponds to a viscosity which is suitable for atomization. Usually, as mentioned before, the concentration is in the range of from 2 to 50 weight-%, preferably from 4 to 10 weight-%. The limits, however, are highly dependent on the individual coating agent used. The average diameter of the particles to be coated is usually in the range of from 100 μ to 600, even to 1000 μ, preferably from 200 μ to 600 μ. The relative humidity of the outlet air should usually not exceed 60%. The temperature of the air, which is used to fluidize the particles to be coated, should be adjusted in consideration of the nature of the particles to be coated.

The quality of the coating is not influenced by the shape of the particles. By use of the process of the invention it is possible to produce a continuous coating on spheres and on irregularly shaped particles as well. Several of the known coating procedures are not well adapted to the coating of irregularly shaped particles which are imperfectly coated, only. Therefore, the present process offers special advantages in connection with the coating of irregularly shaped particles. An example of such irregularly shaped particles is a prilled enzyme product including prilled Alcalase or Alcalase P. When prilled Alcalase is coated in accordance with the invention a product consisting of irregularly shaped particles having a continuous coating is formed. Due to the irregular shape these particles have a very reduced tendency to segregate from the other particles of detergent compositions in powder form.

An additive consisting of spheroidal particles having a density different from the density of the particles of the other components of a powdery detergent composition will have a tendency to segregate from said other par-

ticles and thereby create an inhomogeneous detergent composition. The above irregularly shaped particles therefore offer special advantages.

According to the invention the coating fluid may contain a plasticizer such as triacetin, which is illustrated in the following example 2.

By using glycerol as a plasticizer in the coating fluid coated particles having advantageously low dust levels can be obtained according to the invention.

By using glycerol as a plasticizer in the coating fluid in an amount of up to 60 per cent of the dry weight of the coating or up to the point when the coated particles are beginning to adhere to each other, preferably in an amount in the range of from 10 to 30 per cent of the dry weight of the coating agent, the dust level of the coated particles is reduced significantly which will appear from the following.

In order to give a better understanding of how to correlate the different parameters of the process in order to obtain a relative humidity of the outlet air of less than 100% the following calculation with reference to Example 21 is presented. The inlet air, which was the air in the plant, had the following characteristics:

Temperature: 20°C

Relative humidity: 50% corresponding to 7 g of H_2O/kg air.

The rate of the coating fluid was 1700 ml/min. or 102 litre/hour. The coating fluid had a specific gravity of 1.0 g/cm³ and contained 10% by weight of coating agent, corresponding to a water inlet amount from the coating fluid of 91.8 kg/hour.

The rate of fluidizing air was 8000 N m³/hour or 9600 kg of air/hour. Thus, the fluidizing air introduced $0.007 \times 9600 = 67.2$ kg of water in the system per hour.

Thus, per hour a total of $91.8 + 67.2$ kg of water was introduced into the system. This corresponds to 159.0 kg of water, which was removed from the system together with about 9600 kg of air. As the outlet air had a temperature of between 23° and 27°C this amount of humidity in the outlet air corresponds to a relative humidity in the outlet air of between 95 and 75%. It is noted that this relative humidity is within the limit given for the relative humidity in claim 1.

In order to illustrate the invention further, the following Examples are presented.

Examples 1 to 10 illustrate the preparation of the coating fluid.

Example 1

Methyl cellulose (Methocel MC 15)	50 g
Deionized water	1000 g

The methyl cellulose was triturated with about 333 g of boiling water, after which the rest of the water (optionally cold) was added with stirring. The solution was allowed to stand in a cold place.

Example 2

Methyl cellulose (Methocel MC 15)	50 g
Deionized water	1000 g
Triacetin	5 g

A solution of methyl cellulose and deionized water was prepared as described in Example 1, whereupon the triacetin was added.

Example 3

Sodium carboxymethyl cellulose (Tylose C 10)	50 g
Deionized water	1000 g

The sodium carboxymethyl cellulose was dissolved in the water with stirring, using a high speed mixer.

Example 4

Sodium carboxymethyl cellulose (Tylose C 10)	100 g
Deionized water	1000 g

The sodium carboxymethyl cellulose was dissolved in the water with stirring, using a high speed mixer.

Example 5

Methylhydroxyethyl cellulose (Tylose MH 20)	50 g
Deionized water	1000 g

The methylhydroxyethyl cellulose was dissolved in the water with stirring, using a high speed mixer.

Example 6

Hydroxypropylmethyl cellulose (Methocel XD 1181)	50 g
Deionized water	1000 g

The hydroxypropylmethyl cellulose was dissolved in the water with stirring, using a high speed mixer.

Example 7

Gelatine (Solugel)	50 g
Deionized water	1000 g

The gelatine was dissolved in the water with stirring, using a high speed mixer.

Example 8

Polyvinylpyrrolidone (Kollidon K 25)	50 g
Deionized water	1000 g

The polyvinylpyrrolidone was dissolved in the water with stirring, using a high speed mixer.

Example 9

Polyethylene glycol (Carbowax 4000)	50 g
Deionized water	1000 g

The polyethylene glycol was dissolved in the water with stirring, using a high speed mixer.

Example 10

Polyethylene glycol (Carbowax 6000)	50 g
Deionized water	1000 g

The polyethylene glycol was dissolved in the water with stirring, using a high speed mixer.

The solutions prepared according to Examples 1 to 10 were used for the coating of prilled Alcalase (Alcalase P) in each of four different fluid bed systems as stated in Examples 11 to 14.

Example 11

Apparatus:	"Streba-1" (Aeromatic AG, Basel)
Alcalase P:	1000 g
Nozzle	
Pressure	2 1/2 ato
Internal diameter	0.8 mm
Inlet temperature of fluidizing air:	41°—43°C
Temperature of particulate material:	31—33°C
Feed rate of coating fluid:	6 1/2 ml/min.
Fluidizing air:	8—10 scale units

Example 12

Apparatus:	"WSG-5" (W. Glatt, Haltingen, Germany)
Alcalase P:	6000 g
Nozzle	
Position of jacket:	0.5
Pressure	1 1/2 ato.
Internal diameter:	1.2 mm
Inlet temperature of fluidizing air:	42°—45°C
Temperature of particulate material:	31—33°C
Feed rate of coating fluid:	35 ml/min.
Air velocity:	2 1/2 m/sec.

Example 13

Apparatus:	"WSG-30" (W. Glatt, Haltingen, Germany,)
Alcalase P:	45,000 g
Nozzle	
Position of jacket:	0.3
Pressure:	6 ato.
Internal diameter:	1.8 mm
Inlet temperature of fluidizing air:	42°—45°C
Temperature of particulate material:	31—33°C
Feed rate of coating fluid:	187 ml/min.
Fluidizing air:	5 scale units

Example 14

Apparatus:	"Streba-60" (Aeromatic AG, Basel)
Alcalase P:	135 kg
Nozzle	
Position of jacket	1.0
Pressure:	6 ato.
Internal diameter:	2.3 mm
Inlet temperature of fluidizing air:	42—45°C
Temperature of particulate material:	31—33°C
Feed rate of coating fluid:	325 ml/min.
Rate of fluidizing air:	corresponding to position 3 of damper

In all cases particulate products were produced having remarkably good properties.

The amount of coating layer on the particles and the amount of dust present in some of the coated products prepared according to Examples 12 to 14 appear from the following table II.

TABLE II

Example No.	Coating fluid prepared according to Example No.	Amount of coating layer on coated product	Amount of dust in µg/100 g of product Total	Enzyme
	1	1%	20	2.1
	1	1%	20	1.6
	6	1%	5	0.8
12	1	1/2%	20	2.6
	1	1%	15	1.8
	1	1 1/2%	20	0.8
	6	2%	10	1.1
	6	3%	10	0.8
	1	1%	5	1.8
13	1	1/2%	20	1.0
	1	1%	5	1.0
	1	1%	10	1.6
14	1	1/2%	50	3.4
	1	1%	15	1.6

Examples 15 to 20 illustrate the preparation of a coating fluid containing glycerol and corresponding coating fluids without glycerol.

Example 15

Methyl cellulose (Methocel MC 15)	50 g
Deionized water	950 g

The methyl cellulose was triturated with about 333 g of boiling water, after which the rest of the water (optionally cold) was added with stirring. The solution was allowed to stand in a cold place.

Example 16

Methyl cellulose (Methocel MC 15)	42.5 g
Glycerol	7.5 g
Deionized water	950.0 g

A solution of methyl cellulose and deionized water was prepared as described in Example 15, whereupon the glycerol was added.

Example 17

Sodium carboxymethyl cellulose (Cellofas B 5)	100 g
Deionized water	900 g

The sodium carboxymethyl cellulose was triturated with about 333 g of boiling water, after which the rest of the water (optionally cold) was added with stirring. The solution was allowed to stand in a cold place. The word "Cellofas" is a Trade Mark.

Example 18

Sodium carboxymethyl cellulose (Cellofas B 5)	85 g
Glycerol	15 g
Deionized water	900 g

A solution of sodium carboxymethyl cellulose and deionized water was prepared as described in Example 17, whereupon the glycerol was added.

Example 19

Sodium carboxymethyl cellulose (Cekol HS)	100 g
Deionized water	900 g

A solution of sodium carboxymethyl cellulose and deionized water was prepared as described in Example 17. The word "Cekol" is a Trade Mark.

Example 20

Sodium carboxymethyl cellulose (Cekol HS)	85 g
Glycerol	15 g
Deionized water	900 g

A solution of sodium carboxymethyl cellulose and deionized water was prepared as described in Example 17, whereupon the glycerol was added.

The solutions prepared according to Examples 15 to 20 were used for the coating of Alcalase M in a fluid bed system as stated in Example 21.

Example 21

Apparatus:	"WSG-300 (W. Glatt, Haltingen, Germany)
Alcalase M:	600 kg
Nozzle	six-headed nozzle
Internal diameter:	1.2 mm
Jacket diameter:	6.0 mm
Pressure:	6.0 ato.
Inlet temperature of fluidizing air:	46°—50°C
Temperature of particulate material:	23°—27°C
Feed rate of coating fluid:	1700 ml/min.
Fluidizing air:	8000 N m³/hour

In all cases particulate products are produced having remarkably good properties, especially in regard to the low dust level.

The amount of dust present in the coated products prepared according to Example 21 appears from the following table III.

TABLE III

Example No.	Coating fluid prepared according to Example No.	Amount of coating layer on coated product	Amount of dust in μg/100 g of product Total	Enzyme
	15	1%	20	1.2
	16	1%	10	0.5
	17	1%	15	1.6
21	18	1%	10	0.7
	19	1%	30	1.3
	20	1%	10	0.8

It appears from the above table III that by using glycerol as a plasticizer in the coating fluid a remarkably advantageous effect on the dust level of the coated particles was obtained.

WHAT WE CLAIM IS:—

1. A process for coating water soluble or water dispersible particles by means of the fluid bed technique, which process comprises introduction of the particles to be coated in a fluid bed reactor, the mean diameter of the particles to be coated being in the range of from 0.1 to 0.6 mm, and introduction of a coating material essentially consisting of an aqueous solution or dispersion of a macro-molecular film forming, water soluble or water dispersible coating agent by means of atomization, wherein the relative humidity of outlet air from the fluid bed is below 100% and wherein the maximum size of the atomized droplets of the coating fluid does not exceed the minimum size of the particles to be coated.

2. A process according to Claim 1, wherein the water soluble or water dispersible particles to be coated contain one or more enzymes.

3. A process according to Claim 2, wherein the enzyme or enzymes is/are bacterial proteinases.

4. A process according to Claim 3, wherein the bacterial proteinase(s) is/are precoated in order to reduce dust formation.

5. A process according to Claim 4, wherein the bacterial proteinase(s) is/are microbial proteinase(s).

6. A process according to Claim 3, wherein the bacterial proteinase(s) is/are alkaline resistant proteinase(s) manufactured according to British Patent No. 1,243,784.

7. A process according to Claim 2, wherein the enzyme or enzymes is/are bacterial or fungal carbohydrase(s).

8. A process according to Claim 7, wherein the bacterial carbohydrase(s) is/are thermally stable amylase(s) manufactured according to British Patent No. 1,296,839.

9. A process according to any one of the preceding claims, wherein the macro-molecular film forming, water soluble or water dispersible coating agent is a cellulose derivative.

10. A process according to Claim 9, wherein the cellulose derivative is methyl cellulose, hydroxybutylmethyl cellulose, sodium carboxymethyl cellulose, hydroxyethylmethyl cellulose or hydroxypropylmethyl cellulose.

11. A process according to any one of Claims 1 to 8, wherein the macro-molecular film forming, water soluble or water dispersible coating agent is a polyvinylpyrrolidone.

12. A process according to any one of Claims 1 to 8, wherein the macro-molecular film forming, water soluble or water dispersible coating agent is a polyethylene glycol.

13. A process according to Claim 12, wherein the polyethylene glycol has a mole-

cular weight in the range of from 400 to 6000.

14. A process according to any one of Claims 1 to 8, wherein the macro-molecular film forming, water soluble or water dispersible coating agent is a methacrylic resin.

15. A process according to any one of Claims 1 to 8, wherein the macro-molecular film forming, water soluble or water dispersible coating agent is a gelatine.

16. A process according to any one of the preceding claims, wherein the coating fluid contains a plasticizer.

17. A process according to Claim 16, wherein the plasticizer is glycerol.

18. A process according to Claim 17, wherein the glycerol is used in an amount of up to 60% of the dry weight of the coating agent.

19. A process according to Claim 18, wherein the glycerol is used in an amount in the range of from 10 to 30% of the dry weighr of the coating agent.

20. A process according to any one of Claims 9 to 19, wherein the concentration of the macromolecular film forming, water soluble or water dispersible coating agent in the coating fluid is in the range of from 2 to 50 weight-%.

21. A process according to Claim 20, wherein the concentration of the macromolecular film forming, water soluble or water dispersible coating agent in the coating fluid is in the range of from 4 to 10 weight-%.

22. A process according to any one of the preceding claims, wherein the mean diameter of the particles to be coated is in the range of from 0.2 to 0.6 mm.

23. A process according to any one of the preceding claims, wherein the thickness of the coating layer is in the range of from 0.1 to 10 μ.

24. A process according to Claim 23, wherein the thickness of the coating layer is in the range of from 0.5 to 1 μ.

25. A process according to any one of the preceding claims, wherein the coating operation is performed batchwise.

26. A process for coating, substantially as described in foregoing Examples 11 and 1.

27. A process for coating, substantially as described in foregoing Examples 11 and 2.

28. A process for coating, substantially as described in foregoing Examples 11 and 3.

29. A process for coating, substantially as described in foregoing Examples 11 and 4.

30. A process for coating, substantially as described in foregoing Examples 11 and 5.

31. A process for coating, substantially as described in foregoing Examples 11 and 6.

32. A process for coating, substantially as described in foregoing Examples 11 and 7.

33. A process for coating, substantially as described in foregoing Examples 11 and 8.

34. A process for coating, substantially as described in foregoing Examples 11 and 9.

35. A process for coating, substantially as described in foregoing Examples 11 and 10.

36. A process for coating, substantially as described in foregoing Examples 12 and 1.

37. A process for coating, substantially as described in foregoing Examples 12 and 2.

38. A process for coating, substantially as described in foregoing Examples 12 and 3.

39. A process for coating, substantially as described in foregoing Examples 12 and 4.

40. A process for coating, substantially as described in foregoing Examples 12 and 5.

41. A process for coating, substantially as described in foregoing Examples 12 and 6.

42. A process for coating, substantially as described in foregoing Examples 12 and 7.

43. A process for coating, substantially as described in foregoing Examples 12 and 8.

44. A process for coating, substantially as described in foregoing Examples 12 and 9.

45. A process for coating, substantially as described in foregoing Examples 12 and 10.

46. A process for coating, substantially as described in foregoing Examples 13 and 1.

47. A process for coating, substantially as described in foregoing Examples 13 and 2.

48. A process for coating, substantially as described in foregoing Examples 13 and 3.

49. A process for coating, substantially as described in foregoing Examples 13 and 4.

50. A process for coating, substantially as described in foregoing Examples 13 and 5.

51. A process for coating, substantially as described in foregoing Examples 13 and 6.

52. A process for coating, substantially as described in foregoing Examples 13 and 7.

53. A process for coating, substantially as described in foregoing Examples 13 and 8.

54. A process for coating, substantially as described in foregoing Examples 13 and 9.

55. A process for coating, substantially as described in foregoing Examples 13 and 10.

56. A process for coating, substantially as described in foregoing Examples 14 and 1.

57. A process, for coating, substantially as described in foregoing Examples 14 and 2.

58. A process for coating, substantially as described in foregoing Examples 14 and 3.

59. A process for coating, substantially as described in foregoing Examples 14 and 4.

60. A process for coating, substantially as described in foregoing Examples 14 and 5.

61. A process for coating, substantially as described in foregoing Examples 14 and 6.

62. A process for coating, substantially as described in foregoing Examples 14 and 7.

63. A process for coating, substantially as described in foregoing Examples 14 and 8.

64. A process for coating, substantially as described in foregoing Examples 14 and 9.

65. A process for coating, substantially as described in foregoing Examples 14 and 10.

66. A process for coating, substantially as described in foregoing Examples 21 and 15.

67. A process for coating, substantially as described in foregoing Examples 21 and 16.

68. A process for coating, substantially as described in foregoing Examples 21 and 17.

69. A process for coating, substantially as described in foregoing Examples 21 and 18.

70. A process for coating, substantially as described in foregoing Examples 21 and 19.

71. A process for coating, substantially as described in foregoing Examples 21 and 20.

72. A coated product whenever prepared by the process of any one of the preceding claims.

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